

---

# Quality Assurance

Lucinda M. Garcia  
Donald H. MacQueen

## Introduction

Quality assurance (QA) is a system of activities and processes put in place to ensure that monitoring and measurement data meet user requirements and needs. Quality Control (QC) consists of procedures used to verify that prescribed standards of performance in the monitoring and measurement process are attained. QA requirements for environmental monitoring of DOE facilities are mandated by DOE Orders and guidance. DOE Order 5400.1 identifies QA requirements for radiological effluent and surveillance monitoring and specifies that a QA program consistent with DOE Order 5700.6 be established. The latter Order sets forth policy, requirements, and responsibilities for the establishment and maintenance of plans and actions that assure quality achievement in DOE programs. The DOE *Environmental Regulatory Guide for Radiological Effluent Monitoring and Environmental Surveillance* (U.S. Department of Energy 1991) requires that an Environmental Monitoring Plan be prepared that contains a QA section discussing the applicable elements of the American National Standards Institute/American Society of Mechanical Engineers (ANSI/ASME) NQA-1, Quality Assurance Program Requirements for Nuclear Facilities (ASME 1989).

LLNL conducted QA activities in 1996 at the Livermore site and Site 300 in accordance with a plan based on DOE Order 5700.6C. DOE Order 5700.6C prescribes a risk-based, graded approach to QA. This process promotes the selective application of QA and management controls based on the risk associated with each activity, maximizing the effectiveness and efficiency in resource use.

LLNL environmental sampling is conducted according to procedures published in Appendix A of the LLNL Environmental Monitoring Plan (Tate et al. 1995). Environmental monitoring samples are analyzed by LLNL or commercial laboratories using EPA standard methods when available. When EPA standard methods are not available, custom analytical procedures, usually developed at LLNL, are used. The radiochemical methods used by LLNL laboratories are described in procedures unique to the laboratory performing the analyses. When analyses are performed by independent contractors, LLNL requires that their laboratories be certified by the State of California for the analyses performed for LLNL. In addition, LLNL requires all analytical laboratories to maintain adequate QA programs and documentation of methods.



## Quality Assurance Activities

During 1996, 106 Nonconformance Reports (NCRs) related to environmental monitoring were written. The major sources of NCRs continued to be air particulate sampling equipment failures and analytical laboratory problems. Air particulate sampling equipment was upgraded prior to November 1996 and a significant reduction in the number of NCRs related to that network occurred after those improvements were completed. This trend is expected to continue.

Of 44 NCRs related to analytical laboratories, 26 were associated with one contract laboratory. LLNL personnel were unable to resolve all the issues with that laboratory, and as a result, much of the sample load scheduled to go to that laboratory was diverted to another laboratory pending demonstration of the implementation of effective corrective action. The remaining NCRs written for analytical laboratories resulted from minor start-up or communications problems and were easily resolved.

---

## Analytical Laboratories

In March of 1996, LLNL and Lawrence Berkeley National Laboratory (LBNL) began using new contracts with six off-site analytical laboratories—three for nonradiological analyses of environmental samples, and three for nonradiological analyses of waste samples and radiological analyses of waste and environmental samples. The six initial off-site analytical laboratories were reduced to four as the year progressed because of decreased sample volumes at LLNL and LBNL and changes in key capabilities of two laboratories.

A joint LLNL/LBNL committee called the Analytical Contract Management Team (ACMT) was formed to manage contracts with the analytical laboratories. In addition, an analytical contract forum was created to provide an opportunity for ongoing discussion of contract issues at the worker level. Issues that arise at monthly forum meetings can be raised to the ACMT for resolution. Additionally, contract laboratory representatives are often invited to forum meetings to improve communication and resolve problems.

No analytical laboratory audits were performed in 1996. All off-site analytical laboratories will be audited in early 1997.

## ***Participation in Laboratory Intercomparison Studies***

The LLNL Chemistry and Materials Science Environmental Services Environmental Monitoring Radiation Laboratory (CES EMRL) and the Hazards Control Department's



Analytical Laboratory (HCAL) participated in both the EPA's Environmental Monitoring Systems Laboratory (EMSL) intercomparison studies program and the DOE Environmental Monitoring Laboratory (EML) intercomparison studies program in 1996.

A review of the EMSL data indicates that 41 of 42 analyses performed by the CES EMRL fell within established acceptance control limits, and 7 of 8 sample results from HCAL fell within control limits. Review of the EML results shows that 71 of 71 results from HCAL submitted by the CES EMRL and 10 of 10 results submitted by the HCAL were within the established acceptance control limits. The HCAL also participated in four EPA Water Pollution and Water Supply intercomparison studies for metals during 1996. Seventy-two of 73 determinations of metals in LLNL sewage samples fell within established acceptance control limits.

The intercomparison study results, as well as the follow-up explanation and response for data that fell outside the acceptance control limits are presented in Volume 2, Table 13-4. Contract laboratories are also required to participate in laboratory intercomparison programs; however, permission to publish their results for comparison purposes was not granted for 1996.

The potential effects of unacceptable intercomparison study results on routine data have not been fully determined or evaluated. A joint EPD/CES performance evaluation committee has been formed to create a systematic process for evaluating laboratory performance using traceable standards. A method for evaluating the results of intercomparison studies will be developed by that committee.

---

## Duplicate Analyses

Duplicate or collocated samples are samples collected independently, as close as possible to the same point in space and time, and are intended to be identical in all respects. Collocated samples processed and analyzed by the same organization provide intralaboratory precision information for the entire measurement system, including sample acquisition, homogeneity, handling, shipping, storage, preparation, and analysis. Collocated samples processed and analyzed by different organizations provide interlaboratory precision information for the entire measurement system (U.S. Environmental Protection Agency 1987). Collocated samples may also be used to identify errors—for example, mislabeled samples and data entry errors.

**Tables 13-1 through 13-3** present data generated by collocated sample pairs, grouped by sample matrix and analyte. Samples from both the Livermore site and Site 300 are included. **Tables 13-1 and 13-2** contain data pairs in which both values are above the

detection limit and all radiological results for which a reported value was available. The tables exclude radiological values for which only a minimum detectable activity was reported. In addition, **Table 13-2** excludes radiological results for which the reported value was negative. **Table 13-3** contains data pairs in which either or both values are below the detection limit.

If there were more than eight data pairs with both results above the detection limit, precision and regression analyses were performed; the results are presented in **Table 13-1**. Precision is measured by the percent relative standard deviation (%RSD); see the EPA *Data Quality Objectives for Remedial Response Activities: Development Process*, Section 4.6 (U.S. Environmental Protection Agency 1987).

Acceptable values for %RSD vary greatly with matrix, analyte, and analytical method; however, values above 30% are common. The results for %RSD given in **Table 13-1** are the 75th percentile of the individual precision values. Regression analysis consists of fitting a straight line to the collocated sample pairs. Good agreement is indicated when the data lie close to a line with slope equal to one and intercept equal to zero, as illustrated in **Figure 13-1**. Allowing for normal analytical variation, the slope of the fitted line should be between 0.7 and 1.3, and the absolute value of the intercept should be less than the detection limit. The coefficient of determination ( $r^2$ ) should be  $>0.8$ .

If there are eight or fewer data pairs with both results above the detection limit, the ratios of the individual duplicate sample pairs are averaged; the average, minimum, and maximum ratios for selected analytes are given in **Table 13-2**. The mean ratio should be between 0.7 and 1.3.

If one of the results in a pair is below the detection limit, then the other result should be less than two times the detection limit. **Table 13-3** identifies the sample media and analytes for which at least one pair failed this criterion. Analytes with fewer than four pairs total are omitted from the table.

These analyses show generally good agreement between routine samples and quality assurance duplicates: approximately 84% of the pairs have a precision better than 30%. Data sets not meeting our precision criteria generally fall into one of two categories. The first category, outliers, can occur because of data transcription errors, measurement errors, or real but anomalous results. Of 34 data sets reported in **Table 13-1**, five did not meet the criterion for acceptability because of outliers. **Figure 13-2** illustrates a set of collocated pairs with two outliers. The other category of results that does not meet the criterion for acceptability consists of data sets in which there is a lot of scatter. This tends to be typical of measurements at extremely low concentrations as illustrated in **Figure 13-3**.

**Table 13-1.** Quality assurance duplicate sampling. Summary statistics for analytes with more than eight pairs in which both results were above the detection limit.

Medium	Analyte	N <sup>(a)</sup>	%RSD <sup>(b)</sup>	Slope	r <sup>2(c)</sup>	Intercept
<b>Air</b>	Beryllium <sup>(d)</sup>	10	18.4	0.733	0.41	2.7 (pg/m <sup>3</sup> )
	Gross alpha <sup>(d)</sup>	96	73.1	0.125	0.013	$2.80 \times 10^{-7}$ (pCi/L)
	Gross beta <sup>(e)</sup>	96	27.8	0.869	0.78	$1.089 \times 10^{-6}$ (pCi/L)
	Plutonium-239 <sup>(e)</sup>	12	88.7	3.10	0.67	$-97 \times 10^{-12}$ (pCi/L)
	Tritium	41	22.7	0.983	0.97	-0.000139 (pCi/L) (air)
<b>Radiation dose</b>	Radiation dose	32	4.43	0.875	0.89	1.70 (mrem)
<b>Ground water</b>	Arsenic	19	9.43	0.930	0.99	0.000022 (mg/L)
	Barium	13	3.72	1.00	0.87	0.006314 (mg/L)
	Bicarbonate alkalinity (as CaCO <sub>3</sub> )	9	11.3	1.24	0.83	-62.3 (mg/L)
	Calcium	9	2.21	0.958	1.0	1.18 (mg/L)
	Chloride	11	18.4	0.827	0.96	13.1 (mg/L)
	Fluoride <sup>(e)</sup>	11	1.63	0.715	0.76	0.196 (mg/L)
	Gross alpha <sup>(d)</sup>	25	63.3	0.557	0.62	0.476 (pCi/L)
	Gross beta <sup>(d)</sup>	25	45.4	0.751	0.51	1.23 (pCi/L)
	Magnesium	9	3.82	0.924	0.99	0.231 (mg/L)
	Nitrate (as N) <sup>(e)</sup>	15	28.3	1.30	0.48	-2.11 (mg/L)
	Nitrate (as NO <sub>3</sub> ) <sup>(e)</sup>	17	13.1	0.694	0.71	5.52 (mg/L)
	Potassium	9	3.82	0.924	0.99	0.231 (mg/L)
	Radium-226 <sup>(d)</sup>	13		1.14	0.68	0.135 pCi/L
	Sodium	10	3.93	0.985	0.99	0.291 (mg/L)
	Specific conductance	11	3.82	0.981	0.94	52.7 (μmho/cm)
	Sulfate	11	4.04	0.943	1.0	1.39 (mg/L)
	TDS	9	1.63	1.01	1.0	-11.5 (mg/L)
	Total alkalinity (as CaCO <sub>3</sub> )	9	11.3	1.24	0.83	-62.3(mg/L)
	Total hardness (as CaCO <sub>3</sub> )	9	5.41	0.986	1.0	-5.99(mg/L)
	Tritium	9	35.2	0.994	1.0	3.68 (pCi/L)
	Uranium-234 and uranium-233	12	17.8	0.866	0.93	0.329 (pCi/L)
	Uranium-235 and uranium-236 <sup>(d)</sup>	12	32.2	0.788	0.72	0.0375 (pCi/L)
	Uranium-238	12	18.0	0.786	0.99	0.367 (pCi/L)
	Vanadium	10	2.48	0.967	0.99	0.001448 (mg/L)
	pH <sup>(d)</sup>	9	0.975	0.494	0.52	3.87 Units

**Table 13-1.** Quality assurance duplicate sampling. Summary statistics for analytes with more than eight pairs in which both results were above the detection limit (concluded).

Medium	Analyte	N <sup>(a)</sup>	%RSD <sup>(b)</sup>	Slope	r <sup>2(c)</sup>	Intercept
Sewer	Gross alpha <sup>(d)</sup>	52	94.8	0.500	0.17	0.684 (pCi/L)
	Gross beta	52	17.4	0.898	0.97	2.10 (pCi/L)
	Tritium	52	65.6	1.00	1.0	18.2 (pCi/L)

<sup>a</sup> Number of duplicate pairs included in regression analysis.

<sup>b</sup> 75th percentile of percent relative standard deviation (%RSD), where  $\%RSD = \left( \frac{200}{\sqrt{2}} \right) \left( \frac{|x_1 - x_2|}{x_1 + x_2} \right)$  and  $x_1$  and  $x_2$  are the reported concentrations of each routine-duplicate pair.

<sup>c</sup> Coefficient of determination.

<sup>d</sup> Outside acceptable range of slope or  $r^2$  due to variability.

<sup>e</sup> Outside acceptable range of slope or  $r^2$  due to outliers.

**Table 13-2.** Quality assurance duplicate sampling. Summary statistics for selected analytes with eight or fewer pairs in which both results were above the detection limit.

Media	Analyte	N <sup>(a)</sup>	Mean ratio	Minimum ratio	Maximum ratio
Aqueous	Gross alpha <sup>(b)</sup>	2	1.6	0.43	2.8
	Gross beta	4	0.96	0.12	1.8
	Tritium	2	0.95	0.88	1.0
Ground water	Chromium	8	0.99	0.46	1.3
	Thorium-232 <sup>(b)</sup>	2	4.8	0.77	8.8
	Trichloroethene	7	0.95	0.77	1.1
Rain	Tritium	3	1.3	0.87	2.1
Runoff (from rain)	Gross alpha <sup>(b)</sup>	7	150	0.37	1000
	Gross beta <sup>(b)</sup>	7	2.5	0.92	8.3
	Tritium	3	1.2	1.1	1.3
Soil	Beryllium	1	1.7	1.7	1.7
	Cesium-137	4	0.82	0.30	1.1
	Plutonium-239	4	0.92	0.65	1.2
Vegetation	Tritium	6	0.80	0.15	1.7
VG	Tritium, per gram dry weight	6	0.69	0.12	1.5

<sup>a</sup> Number of data pairs.

<sup>b</sup> Outside acceptable range of 0.7–1.3, for mean ratio.

**Table 13-3.** Quality assurance duplicate sampling. Summary statistics for analytes with at least four pairs in which one or both results were below the detection limit.

Medium	Analyte	Number of inconsistent pairs	Number of pairs	Percent of inconsistent pairs
Other water	Zinc	1	4	25
Ground water	Arsenic	2	7	29
	Chromium	1	16	69
	Copper	1	27	4
	Lead	1	38	3
	Nickel	1	26	4
	Nitrate (as NO <sub>3</sub> )	1	5	20
	Orthophosphate	1	7	14
	Selenium	1	19	5
	Tritium	1	16	6
Soil	Cobalt-60	1	4	25

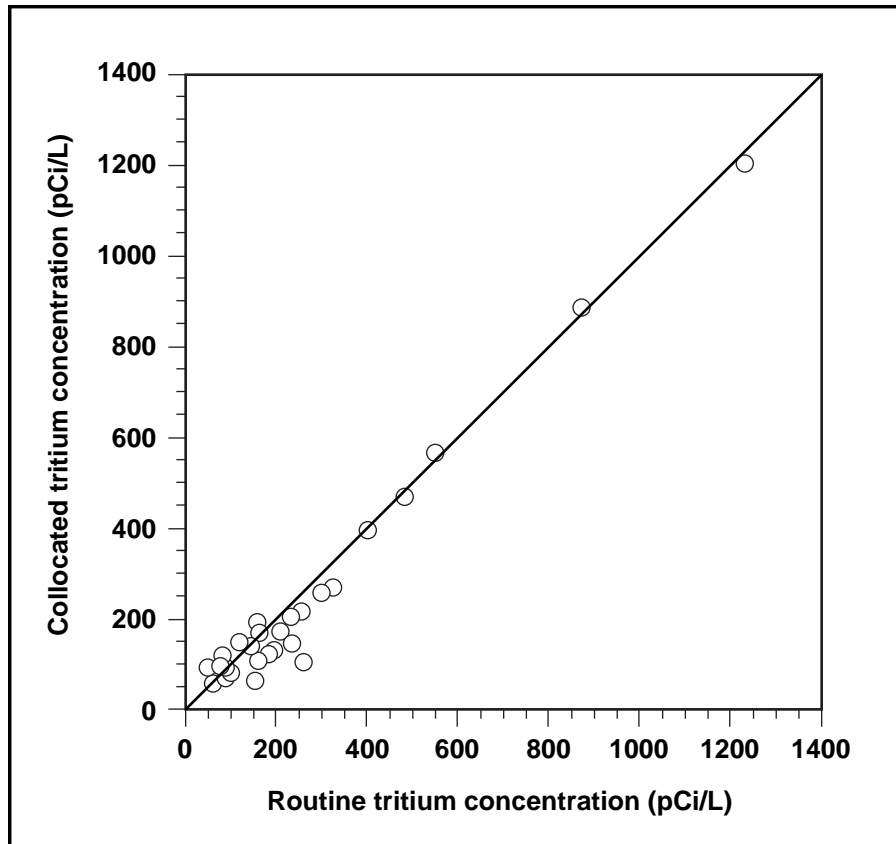
Low concentrations of radionuclides on particulates in air highlight this effect even more because one or two radionuclide-containing particles on an air filter can significantly impact results. Another cause of high variability is sampling and analytical methodology. Analyses of total organic carbon and total organic halides in water are particularly difficult to control. Of the 34 data sets in **Table 13-1**, eight show sufficient variability in results to make them fall outside of the acceptable range.

## Deviations and Changes to the Sampling Program

The sections that follow summarize changes to the environmental sampling effort made during 1996, deviations from planned environmental sampling, and omissions of data expected from regularly scheduled samples.

### ***Changes to Environmental Monitoring Networks***

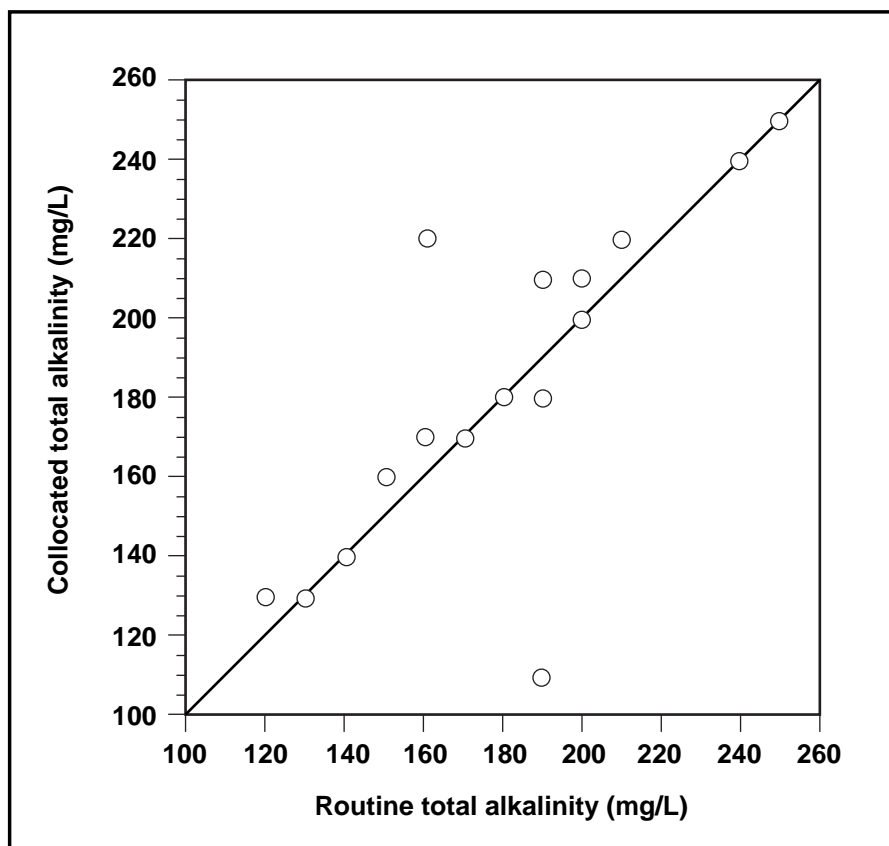
Changes that were made to environmental monitoring networks in 1996 are summarized in **Table 13-4**.



**Figure 13-1.** Tritium concentration in air from collocated samples. Data are shown with a line having a slope equal to one and an intercept equal to zero. The measure of acceptability is determined by how well the data fall on the line.

The LLNL environmental monitoring program uses alphanumeric location designator codes to define sampling locations. Tables 13-1 to 13-3 in Chapter 13, Volume 2 decode these sampling location designators and provide a cross-reference between current designators and those used in previous years. Changes made in 1996 are noted on those tables.

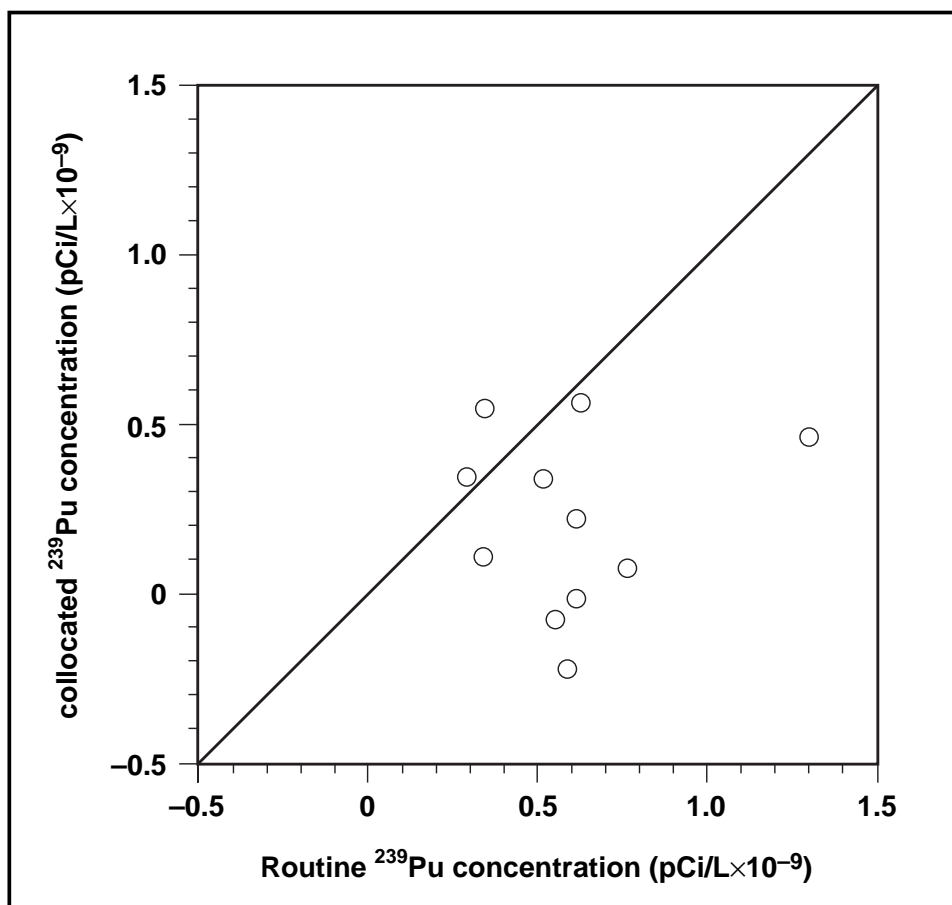
Air tritium sampling location L-HOSP was added to replace a location that was previously monitored by SNL/California. LLNL decided to continue sampling at that location to ensure complete monitoring of environmental tritium in and around the Livermore site.



**Figure 13-2.** Total alkalinity concentration in ground water from collocated samples. Data are shown with a line having a slope equal to one and an intercept equal to zero. This data illustrates the case where the data fit the line well, except for two outliers.

Vegetation sampling location L-RAIL was replaced with location L-NPER in the first quarter of 1996 because of difficulty in accessing the RAIL site. Vegetation sampling began at the 3-PRIM location at Site 300 during the fourth quarter of 1996. 3-PRIM vegetation data will improve LLNL's ability to evaluate the dose to the public by complementing air sampling (to be added in 1997) at PRIMEX/Physics International, location of the sitewide maximally exposed individual (see Chapter 12).

Twelve cooling towers were removed from the monitoring network during 1996. This was done because these towers are currently operating under a waiver and have been dropped from the NPDES permit because they are being discharged to percolation pits. If discharge from these towers to surface waters resumes, they will be included in the monitoring network.



**Figure 13-3.** Plutonium-239 concentration on air filters from collocated samples. Data are shown with a line having a slope equal to one and an intercept equal to zero. This data illustrates the inherent variability of measurements at extremely low concentrations.

The WDR-96-248 monitoring network was created in response to monitoring requirements specified in 1996 amendments to an existing permit.

### ***Explanation of Missing Samples***

Planned samples and actual samples collected and analyzed in 1996 are summarized in **Table 13-5**.

**Table 13-4.** Changes to environmental monitoring networks in 1996.

Environmental medium	Livermore site	Site 300
Air particulate	No changes	No changes
Air tritium	Added location L-HOSP in 11/96	Not sampled
Soil	No changes	No changes
Arroyo sediment	No changes	Not sampled
Vegetation	Dropped location L-RAIL prior to the beginning of 1996 and replaced it with L-NPER Added locations PIN1 and PIN2 in the 4th quarter.	Added location 3-PRIM in fourth quarter of 1996
Wine	No changes	Not sampled
Rain	No changes	No changes
Storm water runoff	No changes	Renamed 3-CARN to 3-CARW during 1996
Drainage Retention Basin	No changes	Not applicable
Other surface water	No changes	No changes
Ground water	No changes	WDR 96-248 changes
Cooling towers	Not sampled	Dropped 12 towers prior to the beginning of 1996
Sewage	No changes	Now sampling under WDR 96-248
Thermoluminescent dosimeters	No changes	No changes
Process wastewater	Not sampled	Added new monitoring network during 1996 (WDR 96-248)

Loss of samples for the air particulate network was caused by a number of factors: tripped ground fault interrupt (GFI) circuits (33%), motor problems (30%), flow out of acceptable range (17%), movement of the QC duplicate sampler at the incorrect time (7%), and access or power problems (6%). Lost samples for the air tritium network were due to motor problems (25%), broken flasks (17%), tripped GFI circuits (17%), flow out of acceptable range (8%), and undetermined causes (33%).

Drainage Retention Basin field measurements were missed because of equipment failure or workload and scheduling problems. Field measurements are less important than sampling results for this medium, so the low value of completeness is not a major concern. The lost sample for the Drainage Retention Basin was a QC duplicate that was inadvertently omitted.

**Table 13-5.** Sampling completeness in 1996, Livermore site and Site 300.

Environmental medium	Number of samples planned	Number of samples analyzed	Completeness (percent)
Air particulate			
Gross alpha/beta	1421	1378	97.0
Plutonium	264	264	100
Gamma	24	24	100
Uranium	84	84	100
Beryllium	228	228	100
Air tritium	475	463	97.5
Soil			
Livermore	46	46	100
Site 300	30	30	100
Arroyo sediment (Livermore only)	54	42	77.8
Vegetation			
Livermore	60	60	100
Site 300	29	29	100
Wine	22	22	100
Rain			
Livermore	80	80	100
Site 300	7	0	0
Storm water runoff			
Livermore	490	434	88.6
Site 300	240	115	47.9
Drainage Retention Basin			
Field measurements	416	320	76.9
Samples	107	106	99.1
Other surface water (Livermore only)	70	70	100
Ground water			
Livermore	422	422	100
Site 300	2250	2250	100
Sewage	656	649	98.9
Thermoluminescent dosimeters			
Livermore	172	170	98.8
Site 300	72	63	87.5
Cooling towers (Site 300 only)	34	34	100



The primary cause of sample loss for storm water runoff sampling, both at Livermore and at Site 300, was insufficient flow. One Livermore sampling did not have adequate flow for sampling during three of the four storms sampled. At Site 300, four of seven locations did not exhibit sufficient flow during the first storm sampled, one of seven was not flowing during the second storm, five of seven were not flowing during the third storm, and five of seven were not flowing during the fourth storm. In addition, one Livermore and two Site 300 runoff sample bottles were found to be broken upon receipt at the analytical laboratory.

No Site 300 rain samples were collected during 1996. Site 300 personnel are supposed to collect composite samples that are picked up monthly by environmental monitoring personnel. Due to communication and scheduling problems, the samples were neither collected nor picked up, and the problem was not discovered until after the end of the rainy season. Collection of rain samples at Site 300 will resume in 1997.

Sewer sample losses were caused by equipment problems (57%), over-chlorination of samples (29%), and sampling technologist error (14%).

Thermoluminescent dosimeters were lost when they were destroyed by vandals or eaten by cows. Because the majority of these samples are located off site, it is difficult to protect them from people or animals. Unfortunately, these dosimeters have proven to be particularly appetizing to cows.

---

## Statistical Methods

Statistical methods used in this report have been implemented pursuant to the *Environmental Monitoring Plan* (Tate et al. 1995). These methods reduce the large volumes of monitoring data to summary concentration estimates that are suitable for both temporal and spatial comparisons. Attention is given to estimating accuracy, bias, and precision of all data.

Data review and analyses are conducted in accordance with the *Environmental Monitoring Plan* and the Environmental Monitoring Section's Data Analysis Procedure. These documents contain detailed information regarding the acceptability of data and the procedures that are followed for the identification, notification, and correction of suspect data.

### ***Radiological Data***

The precision of radiological analytical results is displayed in the Volume 2 data tables as the  $2\sigma$  counting error. The counting errors are not used in any summary statistic calculations. By convention, any radiological result exhibiting a  $2\sigma$  counting error greater than or equal to 100% is considered to be indistinguishable from zero. The reported concentration is derived from the number of sample counts minus the number of background counts. A sample with a low or zero concentration may therefore be reported to have a negative value; such results are reported in the tables and used in the calculation of summary statistics and statistical comparisons. Some analytical laboratory reports provide a minimum detectable activity rather than a reported value when the radiological result is below the detection criterion. In this case, the result is presented in the tables with a less-than symbol (<) to indicate its status.

### ***Nonradiological Data***

Nonradiological data that are reported as being below the analytical detection limit also are displayed in the tables with a less-than symbol. The actual detection limit values are used in the calculation of summary statistics as explained below.

### ***Statistical Comparisons***

Standard comparison techniques (such as regression, t-tests, and analysis of variance) have been used where appropriate to determine the statistical significance of trends or differences between means. All such tests of significance have been performed at the 0.05 level. When such a comparison is made, it is explicitly stated in the text as being “statistically significant” or “not statistically significant.” Other uses of the word “significant” in the text do not imply that statistical tests have been performed. These uses instead relate to the concept of practical significance and are based on professional judgment.

### ***Summary Statistics***

Determinations of measures of central tendency and associated measures of dispersion are calculated according to the Environmental Monitoring Plan (Tate et al. 1995). For data sets not containing values below the detection criterion, the measures of central tendency and dispersion are the median and interquartile range (IQR). The IQR is the range that encompasses the middle 50% of the data set. Radiological data sets that include values less than zero may have an IQR greater than the median.

For data sets with one or more, but fewer than one half, values below the detection criterion, the measure of central tendency is the median. If the values of the detection limits and the number of values below the detection limit permit (determined on a case-by-case basis), dispersion is reported as the IQR. Otherwise, no measure of dispersion



is reported. Statistics are calculated using the reported detection limit value for nonradiological data or the reported value for radiological data.

For data sets with one half or more of the values below the detection criterion, the central tendency is reported as less than the median value. Dispersion is not reported.

### ***Radiation Units***

Data for 1995 have been reported in Système Internationale (SI) units to conform with standard scientific practices and federal law. Values in the text are reported in becquerels (Bq) and millisieverts (mSv); equivalent values in picocuries (pCi) and millirems (mrem) are given in parentheses.